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Drinking water monitoring with voltammetric sensors

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Abstract

Pulsed voltammetry has been applied to drinking water monitoring. This non-selective technique facilitates detection of several different threats to the drinking water. A multivariate algorithm shows that anomaly detection is possible with a minimum of false alarms. Multivariate analysis can also be used to classify different types of substances added to the drinking water. Low concentrations of sewage water contaminating the drinking water can be detected. A network of such sensors is envisaged to facilitate real-time and on-line monitoring of drinking water distribution networks.

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Keywords: Voltammetry; drinking water; chemical sensor; anomaly detection; multivariate analysis

1. Introduction

Safe drinking water supply is an important part of a city's critical infrastructure that may be vulnerable to terrorist attacks as well as the constant risk of contamination by accidents and infrastructure breakdowns. Real-time monitoring of drinking water quality in the distribution networks occurs rarely today, but several sensor technologies have been considered for anomaly detection [1-3]. We report here on pulsed voltammetry measurements with an "electronic tongue" [4, 5]. By utilizing this type of non-selective sensor, we are able to detect a plurality of anomalies without the need of a specific sensor for each type of event. Multivariate evaluation techniques facilitate classification of different contaminants. These properties, combined with the robustness of the sensor, make it a potential candidate for relatively maintenance free monitoring of drinking water distribution networks.

2. Experimental details

The voltammetric sensor contains an array of working electrodes and a counter electrode, also called reference electrode in two electrode systems [6]. We have used working electrodes of Au, Pt and Rh, each with 1 mm diameter, and a large area counter electrode of stainless steel. The measurement principle is based on pulsed voltammetry, where a series of voltage pulses are applied and the induced current responses are measured, see Fig. 1a. The size and the shape of the resulting current responses depend on the conductivity, the concentration and type of redox active components, the diffusion coefficients of charged components, the applied voltage and on the working electrode material. Therefore different substances added to the water can often be classified by applying multivariate evaluation techniques. We have used feature extraction and principal component analysis (PCA) in the classification work.

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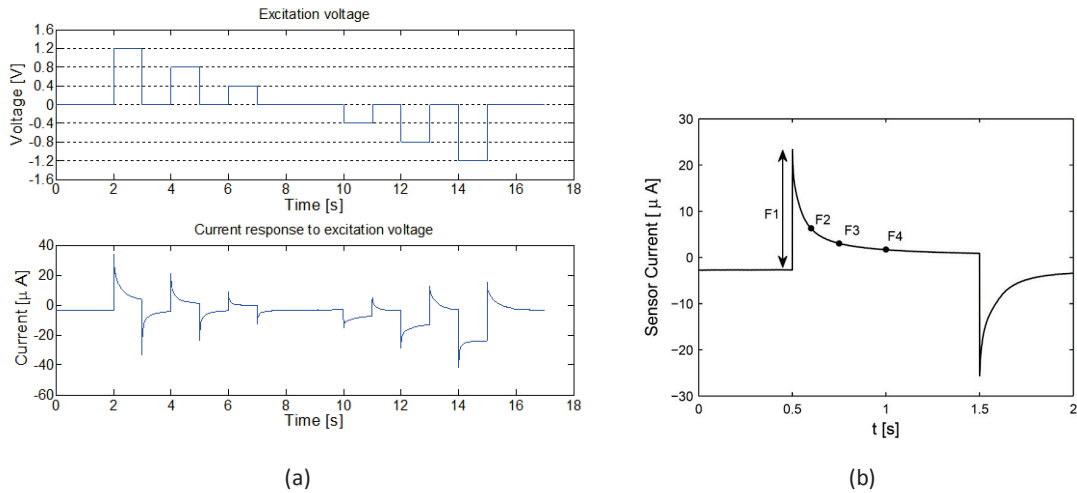


Fig. 1. (a) Excitation voltages (top) and resulting current responses (bottom) in a typical measurement of non-contaminated drinking water in a pilot system with similar properties as the real drinking water distribution system. (b) Current response due to one of the voltage pulses in (a). The positive current transient is due to the sudden increase in voltage and the negative current transient to the sudden decrease. The exact shape of the current transients depends on several parameters, such as the type and concentration of substances added to the drinking water. F1-F4 are examples of features that are extracted from the sensor signals.

3. Results and discussion

From the sensor signals certain features are chosen from the data as illustrated in Fig. 1b. The feature extraction is an initial signal processing step that aims at giving measurement data a compact and informative representation. The electrode signals are sampled at 1000 Hz, and every electrode thus yields a signal vector with 17000 elements in this case. This number indeed needs to be reduced to facilitate statistical modeling and visualization. Exponential functions are therefore fitted to the electrode signals. Every voltage step response is then modeled by

$$y(t) = a + b_1 \exp(c_1 t) + b_2 \exp(c_2 t) + b_3 \exp(c_3 t)$$

which is fitted to the sensor data using numerically and computationally efficient separable least squares techniques. Apart from compressing data, the exponential functions also suppress disturbances. F2-F4 in Fig. 1b are extracted from the exponential functions and they are thereby subjected to noise filtering. F1 is calculated directly from raw data since there is little motivation to filter this very transient part of the signal.

These initial features sum up to 48 (4 features times 12 voltage steps (two for each pulse, see Fig. 1a)) for a whole electrode measurement. To reduce the feature space further and to avoid co-linearity, the first three principal components of a PCA constitute the final feature set.

Anomaly detection is essentially about to learn how the extracted features respond over time to normal (harmless) variations, to be able to detect the deviating signal patterns that result from water pollutions. It is assumed that a measurement on clean water is sampled from a multivariate normal distribution. If the mean and covariance of this distribution is at least approximately known, every measurement can be evaluated by the normal distribution probability density function (PDF) as being more or less likely to be due to clean water:

$$L(x) = \frac{1}{(2\pi)^{p/2} |C|^{1/2}} \exp\left(-\frac{1}{2}(x - m)^T C^{-1}(x - m)\right)$$

$L(x)$ is the likelihood of measurement x and p is the dimension of x . C and m are the covariance and mean of the clean water (normal) distribution $N(m, C)$. If the likelihood $L(x)$ is close to zero, x is unlikely to be a sample of the normal distribution, and the water is probably polluted.

The normal variations in the drinking water characteristics are due to e.g. variations in temperature, water flow velocity, pH, turbidity and residual chlorine. The biggest challenge in this respect turned out to be the temperature variations. Fig. 2 illustrates the influence of the temperature variations on the sensor signal and how it could be handled by introducing a temperature sensor. Fig 2a shows the strong influence of the temperature variations on the raw sensor signal. By first training the anomaly algorithm with data during the normal variations, it was then possible

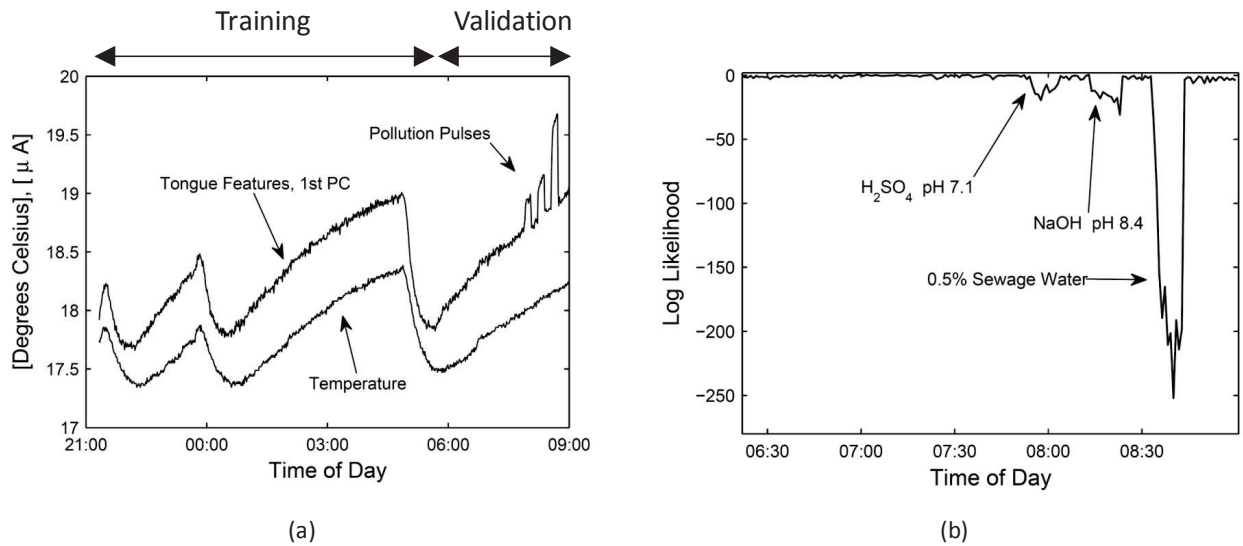


Fig. 2. (a) The first principal component (PC) of extracted features of the Rh electrode signals and temperature measurement data. At the end of the measurement, three pulses of different pollutants are added: H₂SO₄ (changing the pH from 8.2 to 7.1), NaOH (changing the pH from 8.2 to 8.4) and, finally, 0.5 % sewage water. (b) The first 9 h from the 12 h data set of (a) (the "Training" part) have first been used to train a statistical model for change detection. The model is then applied to the final 3 h of the data set (the "Validation" part of (a)). Since the pollution measurements do not fit the model well, they appear very unlikely, and therefore deviate strongly from the background level.

to validate the algorithm with measurements where contaminations were added to the water. As can be seen in Fig. 2b the algorithm detects anomalies only during the contamination pulses and is not confused by the temperature variations. 0.5 % sewage water added to the drinking water can easily be detected in this way and the detection limit is at present about a tenth of this value.

The three electrodes were measured in series in the experiments above and required 17 s per pulse train which means that the total measurement time was almost one minute per sample. Since the work aims at realtime monitoring we reduced the time per voltage pulse of the pulse train and applied parallel measurement of the three electrodes. In this way the sample time could be reduced to 10 s including data communication with an "analysis computer" over the Internet. Fig. 3 illustrates the voltage pulse train and a few raw data responses for different contaminations added to the drinking water. Also in this case a number of features were chosen from the current signals from the three electrodes and a new algorithm for anomaly detection was developed. Fig. 4 shows a long term test (45 days) where measurement data has been collected on natural tap water for several days before low concentrations of sewage water, NaOH, and H₂SO₄ are added. Every new measurement is compared to the set of measurements collected from the past

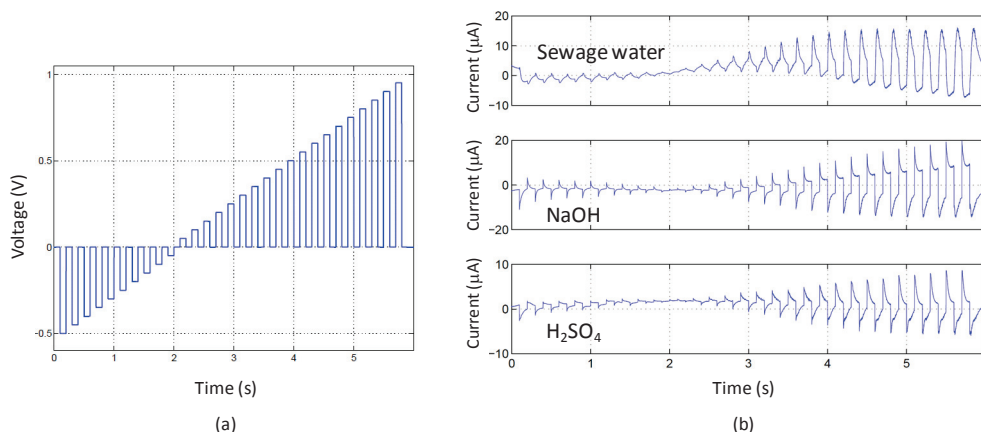


Fig. 3. Measurements with reduced time for pulses and pulse train. (a) Applied voltage pulse train and (b) current responses for the Pt electrode when low concentrations of sewage water, NaOH and H₂SO₄ have been added to drinking water.

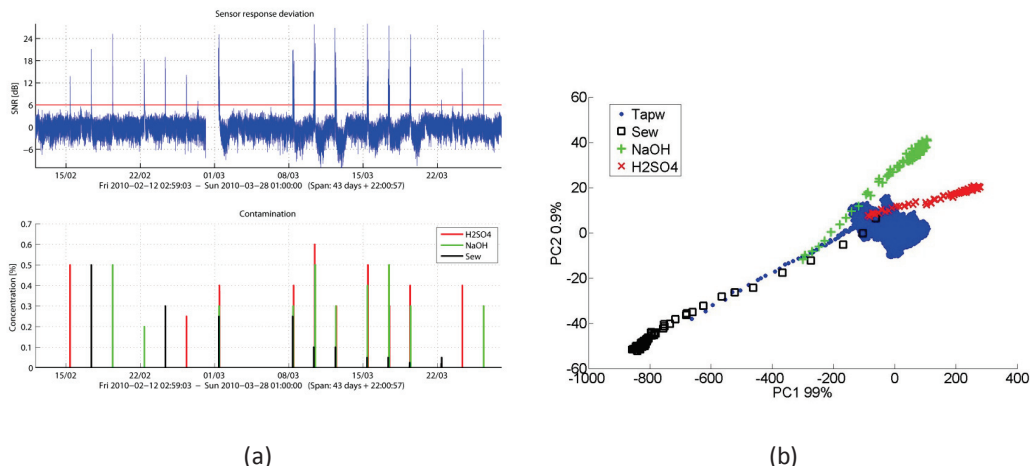


Fig. 4. (a) Long term investigation of the anomaly algorithm. The lower panel shows addition of different concentrations of sewage water (black), NaOH (green) and H_2SO_4 (red) to the drinking water in a pilot system at several occasions during a measurement period of 45 days. The upper panel shows the anomaly signal (blue) and a threshold level (red) placed at 6 dB. (b) Classification of the different pollutants added to the drinking water with PCA. Drinking water (blue) is the reference medium. Addition of sewage water (0.25 %, black) results in data taking off in a completely different direction than those of NaOH (0.3 % (pH increases from 7.7 to 9.4), green) and H_2SO_4 (0.4 % (pH decreases from 7.7 to 7.0), red).

24 hours. The model thus adapts to slow changes of the background due to e.g. drift in the sensor signals. This comparison consecutively gives deviation values that we here choose to express as signal to noise ratio (SNR) in dB, calculated as

$$SNR_t = 10 \log(y_t - m_t)^T R_t^{-1} (y_t - m_t)$$

Here, t denotes time index, y_t the measurement, m_t and R_t the estimated mean and covariance based on the measurements collected 24 hours prior to t . The output of this algorithm is illustrated in Fig. 4a where a long term test (45 days) shows that the algorithm produces alarms when different pollutants are added to the water with a minimum of false alarms in between. Fig. 4b illustrates that a classification of the different substances with PCA is possible.

4. Conclusions

The sensor system can thus alert when anomalies are detected and indicate if the anomaly is, or is not, included in a library of pollutants that the system has been trained for. A network of voltammetric sensors distributed on the drinking water network is envisaged to give a fast alarm, determine which part of the distribution network that is affected, facilitate a forecast of the spreading of the pollution and pinpoint the location of the pollution source. Demonstration measurements over the internet have also been performed, including remote data analysis and remote integration with a crises management system, all in real-time.

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